DECLARATION

I, Yoshito Fukushima of 6th Floor, Esaka Mitaka Bldg., 4-1, Hiroshiba-cho, Suita-shi, Osaka 564-0052, JAPAN, do solemnly and sincerely declare that I understand the Japanese language and the English language well, and that the attached English version is a full, true and faithful translation made by me of the Japanese Patent Application No. 2003-091398.

I make this solemn declaration conscientiously believing the same to be true.

Dated this 26th day of May, 2005

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【Attached Documents】

【Item】	Specification	1
【Item】	Drawings	1
【Item】	Abstract	1
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【Requirement of Proof】 Yes

[Document Name] Scope of Claim for Patent

[Claim 1] A solid electrolytic capacitor, characterized by comprising a substrate composed of niobium having a surface on which a niobium nitride layer is formed, and wherein a dielectric layer composed of niobium oxide is formed on the surface of said niobium nitride layer.

[Claim 2] The solid electrolytic capacitor according to claim 1 or 2, characterized in that

said substrate and said niobium nitride layer constitute an anode.

[Claim 3] The solid electrolytic capacitor according to claim 1 or 2, characterized in that

said dielectric layer is nitrogen-free.

[Claim 4] The solid electrolytic capacitor according to any one of claims 1 to 3, characterized in that

said niobium nitride layer is substantially composed of Nb_2N.

[Claim 5] The solid electrolytic capacitor according to any one of claims 1 to 4, characterized in that

the nitrogen content based on the total weight of said substrate, said niobium nitride, and said dielectric layer is not less than 0.001 % by weight nor more than 0.2 % by weight.

[Claim 6] The solid electrolytic capacitor according to any one of claims 1 to 5, characterized in that

the nitrogen content based on the total weight of said substrate, said niobium nitride, and said dielectric layer is not less than 0.001 % by weight nor more than 0.08 % by weight.

[Claim 7] A method of manufacturing a solid electrolytic capacitor, characterized:

forming a dielectric layer composed of niobium oxide by oxidizing a surface of a substrate composed of niobium, forming a niobium nitride layer between said substrate and said dielectric layer by thermally treating said substrate having said dielectric layer formed thereon in a nitrogen atmosphere, and anodizing said dielectric layer.

[Claim 8] The method of manufacturing a solid electrolytic capacitor according to claim 11, characterized in that the temperature in said thermal treatment is not lower than 300℃ nor higher than 920℃.

[Claim 9] The method of manufacturing a solid electrolytic capacitor according to claim 11 or 12, characterized in that the temperature in said thermal treatment is not lower than 300℃ nor higher than 800℃.

[Document Name] Specification

[Title of the Invention] Solid Electrolytic Capacitor and Manufacturing Method Thereof

[Field of the Invention]

[0001]

The present invention relates to a solid electrolytic capacitor and a manufacturing method thereof.

[Prior Art]

[0002]

Niobium has a dielectric constant about 1.8 times as large as that of tantalum which is a material for conventional solid electrolytic capacitors. Therefore, Niobium has been attracted much attention as a material for next-generation, high capacitance solid electrolytic capacitors.

[0003]

However, when the solid electrolytic capacitor is subjected to high heat in a reflow soldering step, oxygen in a dielectric layer including niobium oxide is partly diffused into the anode and the thickness of the dielectric layer is reduced. As a result, leakage current is more likely to be caused in the dielectric layer.

[0004]

In one suggested solid electrolytic capacitor, a niobium nitride region is formed in a niobium oxide layer as a dielectric in order to reduce changes in capacitance caused

by oxygen diffusion in the reflow soldering step during mounting the solid electrolytic capacitor (see Patent Document No. 1).

[0005]

[Patent Document No. 1]

JP 11-329902, A

[Disclosure of the Invention]

[Problems to Be Solved by the Invention]

[0006]

In the conventional solid electrolytic capacitor provided with the nitride as described above, however, leakage current still cannot be sufficiently reduced.

[0007]

It is an object of the present invention to provide a solid electrolytic capacitor with reduced leakage current and a manufacturing method thereof.

[0008]

[Means for Solving the Problems and Effect of Invention]

A solid electrolytic capacitor according to a first invention includes a substrate composed of niobium on having a surface on which a niobium nitride layer is formed, and a dielectric layer composed of niobium oxide is formed on the surface of the niobium nitride layer.

[0009]

In the solid electrolytic capacitor according to the

present invention, the niobium nitride layer exists between the substrate composed of niobium and the dielectric layer composed of niobium oxide. The niobium nitride layer is chemically stable and has high heat resistance. Therefore, oxygen in the dielectric layer can be prevented from partly diffusing into the substrate when heating is carried out in the process of mounting. As a result, the thickness of the dielectric layer can be prevented from being reduced by oxygen diffusion. Consequently, leakage current can be reduced.

[0010]

The substrate and the niobium nitride layer may constitute an anode. The dielectric layer is preferably nitrogen-free. In this way, the oxide region of the dielectric layer and the nitride region of the niobium nitride layer are clearly separated. In this way, the niobium nitride layer is formed densely and homogeneously, so that the niobium nitride layer can surely prevent oxygen in the dielectric layer from partly diffusing into the substrate. Therefore, the thickness of the dielectric layer can surely be prevented from being reduced by oxygen diffusion and leakage current can be even more reduced.

[0011]

The niobium nitride layer is preferably substantially composed of Nb_2N. In this way, the Nb_2N in the niobium nitride

layer can surely prevent oxygen in the dielectric layer from partly diffusing into the substrate. Therefore, the thickness of the dielectric layer can surely be prevented from being reduced by oxygen diffusion, so that leakage current should sufficiently be reduced.

[0012]

The nitrogen content based on the total weight of the substrate, the niobium nitride, and the dielectric layer is preferably not less than 0.001 % by weight nor more than 0.2 % by weight. In this way, the Nb_2N is formed densely and homogeneously in the niobium nitride layer, so that leakage current can sufficiently be reduced.

[0013]

More preferably, the nitrogen content based on the total weight of the substrate, the niobium nitride, and the dielectric layer is not less than 0.001 % by weight nor more than 0.08 % by weight. In this way, the Nb_2N is formed more densely and homogeneously in the niobium nitride layer, so that leakage current can be even more reduced.

[0014]

A solid electrolytic capacitor according to a second invention includes an anode composed of niobium nitride, and a dielectric layer composed of niobium oxide is formed on the surface of the anode.

[0015]

In the solid electrolytic capacitor according to the present invention, the anode is composed of niobium nitride. Niobium nitride that is chemically stable and has high heat resistance can prevent oxygen in the dielectric layer from partly diffusing into the anode when it is heated in the process of mounting. Consequently, the thickness of the dielectric layer can be prevented from being reduced by oxygen diffusion, so that leakage current can be reduced.

[0016]

The temperature in the thermal treatment is preferably not lower than 300℃ nor higher than 920℃. In this way, Nb_2N is formed densely and homogeneously in the niobium nitride layer, so that leakage current can sufficiently be reduced.

[0017]

More preferably, the temperature in the thermal treatment is not lower than 300℃ nor higher than 800℃. In this way, the Nb_2N is formed more densely and homogeneously in the niobium nitride layer, so that leakage current can be even more reduced.

[Embodiments of the Invention]

[0018]

Now, the invention will be described in detail with reference to embodiments, while the invention is by no means limited to the following embodiments and can be modified as required without changing the gist thereof.

[0019]

Fig. 1 is a view of a solid electrolytic capacitor according to a first embodiment of the invention.

As shown in Fig. 1, in the electrolytic capacitor 100, a dielectric layer 2, a conductive polymer layer 3, a carbon layer 4, and a silver paint layer 5 are formed in this order on the surface of an anode 1. The anode 1 comprises a substrate of niobium (hereinafter referred to as "niobium substrate") 1a and a nitride layer 1b of Nb_2N.

[0020]

The silver paint layer 5 is connected with a cathode terminal 8 through a conductive adhesive 6, and the niobium substrate 1a is connected with an anode terminal 7. Mold sheath resin 9 is formed so that the anode and cathode terminals 7 and 8 have their ends externally extended.

[0021]

The niobium substrate 1a is composed of a porous sinter of niobium particles. The porous sinter of niobium particles has a large surface area and therefore allows a large capacitance. The dielectric layer 2 is composed of highly insulating niobium oxide (Nb_2O_5).

[0022]

The conductive polymer layer 3 is composed of conductive polymer such as polypyrrole or polythiophene. Note that according to the embodiment, the conductive polymer

layer 3 is used as electrolyte, but any other material such as manganese dioxide may be used as the electrolyte. The carbon layer 4 is made of carbon paste, and the silver paint layer 5 is made of silver paste produced by mixing silver particles, protective colloid and an organic solvent.

[0023]

Now, a method of manufacturing the solid electrolytic capacitor 100 according to the embodiment of the invention will be described.

[0024]

A niobium substrate 1a of porous sinter is formed by sintering powder of niobium particles. In this case, the niobium particles are welded with one another.

[0025]

Then, the niobium substrate 1a is oxidized in an aqeous solution of phosphoric acid, so that the dielectric layer 2 of niobium oxide (Nb_2O_5) is formed on the surface of the niobium substrate 1a.

[0026]

Then, the niobium substrate 1a having the dielectric layer 2 formed thereon is heated in a nitrogen atmosphere. In this way, the dielectric layer 2 is reduced, so that nitrogen is diffused into the niobium substrate 1a. Consequently, a niobium nitride layer 1b is formed on the surface of the niobium substrate 1a. Then, the niobium

substrate 1a having the niobium nitride layer 1b formed thereon is again oxidized in an aqueous solution of phosphoric acid.

[0027]

Then, the dielectric layer 2 has its surface coated with a conductive polymer layer 3 composed of conductive polymer such as polypyrrole or polythiophene by electrolytic polymerization or vapor phase polymerization. In this case, the conductive polymer layer 3 is formed on the surface of the dielectric layer 2 to fill in gaps in the dielectric layer 2 on the surface of the porous sinter.

[0028]

Then, carbon paste is applied on the conductive polymer layer 3 and a carbon layer 4 is thus formed on the conductive polymer layer 3. Silver paste is applied on the carbon layer 4 and dried at a prescribed temperature, so that a silver paint layer 5 is formed on the carbon layer 4. The silver paint layer 5 is connected with the cathode terminal 8 through a conductive adhesive 6. The niobium substrate 1a is connected with the anode terminal 7.

[0029]

Then, mold sheath resin 9 is formed so that the anode and cathode terminals 7 and 8 have their ends externally extended. By this method, the solid electrolytic capacitor 100 is prepared.

[0030]

In the solid electrolytic capacitor 100, the niobium nitride layer 1b is formed between the niobium substrate 1a and the dielectric layer 2. The niobium nitride layer 1b is chemically stable and has high heat resistance, and therefore oxygen in the dielectric layer 2 can be prevented from partly diffusing into the niobium substrate 1a. Therefore, the thickness of the dielectric layer 2 is not reduced, and leakage current can be reduced.

[0031]

Note that according to the embodiment, the niobium porous sinter is used as the niobium substrate 1a for the solid electrolytic capacitor, but any other type of material such as a niobium film may be used.

[0032]

(Examples)

In the following Inventive Examples 1 to 15, solid electrolytic capacitors were prepared according to the first embodiment described above and evaluated. In the following Inventive Examples 16 to 26, solid electrolytic capacitors according to the second embodiment were prepared and evaluated.

[0033]

(Inventive Example 1)

In Inventive Example 1, a solid electrolytic capacitor

as shown in Fig. 3 was prepared by the following method.

[0034]

(Oxidizing Step 1)

A niobium film as thick as 0.1 mm was used as a niobium substrate 1a. The niobium substrate 1a was allowed to stand for 30 minutes for oxidization in a 0.5 wt% phosphoric acid aqueous solution maintained at 60℃ at a constant voltage of 45 V, and a dielectric layer 2 composed of niobium oxide was formed on the surface of the niobium substrate 1a.

[0035]

(Nitriding Step)

Now, the niobium substrate 1a having the dielectric layer 2 formed thereon was allowed to stand in an electric furnace maintained at 600℃ and 0.1 atmospheric pressure for five minutes. In this way, a niobium nitride layer 1b was formed between the niobium substrate 1a and the dielectric layer 2.

[0036]

(Oxidizing Step 2)

The niobium substrate 1a was oxidized again in a 0.5 wt% phosphoric acid aqueous solution maintained at 60℃. In this way, the capacitor in Inventive Example 1 was prepared.

[0037]

(Comparative Example 1)

In Comparative Example 1, using a niobium substrate

of a niobium film as thick as 0.1 mm which was the same as the niobium substrate 1a in Inventive Example 1, only the oxidizing step 1 in Inventive Example 1 was carried out. In this way, the capacitor in Comparative Example 1 was prepared. More specifically, the capacitor in Comparative Example 1 does not have a niobium nitride layer.

[0038]

(Comparative Example 2)

In Comparative Example 2, a capacitor was prepared according to the following method.

[0039]

(Nitriding Step)

A niobium substrate of a niobium film as thick as 0.1 mm which was the same as the niobium substrate 1a in Inventive Example 1 was thermally treated for five minutes at 600℃ in a nitrogen atmosphere and a niobium nitride layer was thus formed on the surface of the niobium substrate.

[0040]

(Oxidizing Step)

The niobium substrate is oxidized for 30 minutes in a 0.5 wt% phosphoric acid aqueous solution maintained at 60℃ and a constant voltage of 45V and a dielectric layer composed of niobium oxide was formed on the surface of the niobium substrate. In this way, the capacitor in the Comparative Example 2 was prepared.

[0041]

According to the method, niobium nitride should be formed in the dielectric layer composed of niobium oxide (see Patent Document No. 1).

[0042]

(Evaluation)

The nitrogen concentration of the capacitor in Inventive Example 1 was quantitatively analyzed by thermal conductivity method (JIS G 1201). As a result, the capacitor in Inventive Example 1 contained 0.02 wt% nitrogen.

[0043]

Then, the capacitor in Inventive Example 1 was identified by X-ray powder method. As a result, the diffraction patterns of niobium and Nb_2N were observed. Similarly, the capacitor in Comparative Example 2 was identified, and as a result, the diffraction patterns of niobium and Nb_2N were observed.

[0044]

Then, the capacitors in Inventive Example 1 and Comparative Examples 1 and 2 were investigated for the distributed states of niobium, oxygen, and nitrogen by ESCA (Electron Spectroscopy for Chemical Analysis), and leakage current was measured.

[0045]

Figs. 3, 4, and 5 are views showing the measurement

results for the capacitors in Inventive Example 1 and Comparative Examples 1 and 2, respectively. In Figs. 4, 5, and 6, the ordinate represents the contents of elements in each capacitor, and the abscissa represents sputtering time. The sputtering time corresponds to positions in the thickness-wise direction of the capacitor.

[0046]

As shown in Fig. 3, the dielectric layer 2 of the capacitor in Inventive Example 1 contains oxygen and niobium and is nitrogen-free. Meanwhile, the niobium nitride layer 1b contains niobium and nitrogen and is oxygen-free. In this way, in the capacitor in Inventive Example 1, the dielectric layer 2 composed of niobium oxide and the niobium nitride layer 1b are clearly separated.

[0047]

As shown in Fig. 4, the dielectric layer of the capacitor in Comparative Example 1 contains oxygen and niobium and is free from a niobium nitride layer. More specifically, the dielectric layer is directly formed on the surface of the niobium substrate.

[0048]

As shown in Fig. 5, the dielectric layer of the capacitor in Comparative Example 2 contains oxygen, nitrogen, and niobium. The oxygen content is reduced and the nitrogen content increases from the surface to the inner

side. More specifically, the capacitor in Comparative Example 2 has a region where both oxygen and nitrogen exist, in other words, the niobium oxide and the niobium nitride both exist.

[0049]

Leakage current in the capacitors in Inventive Example 1 and Comparative Examples 1 and 2 after thermal treatment was measured. Fig. 7 is a schematic view of how leakage current in the capacitor in Inventive Example 1 was measured.

[0050]

The capacitor in Inventive Example 1 was thermally treated for 30 minutes at 300℃.

Then, as shown in Fig. 7, a 0.5 wt% phosphoric acid aqueous solution 40 maintained at 60℃ was stored in a container 42, and the thermally treated capacitor in Inventive Example 1 was immersed in the phosphoric acid aqueous solution 40. In this state, a constant voltage of 10 V was applied and leakage current was measured 20 seconds after the application.

[0051]

The capacitors in Comparative Examples 1 and 2 were also measured for leakage current after thermal treatment. The result is shown in Table 1. Note that the respective the leakage current measurement results of the solid electrolytic capacitors of the inventive example 1 and

comparative examples 1 and 2 are normalized by the leakage current measurement result of the solid electrolytic capacitor of the inventive example 1 as 100,and the normalized the leakage current values are represented in

[0052]

[Table 1]

	leakage current
Inventive Example 1	100
Comparative Example 1	1000
Comparative Example 2	600

[0053]

As shown in Table 1, leakage current ten times as large as that of the capacitor in Inventive Example 1 was caused in the capacitor in Comparative Example 1. Leakage current six times as large as that of the capacitor in Inventive Example 1 was caused in the capacitor in Comparative Example 2. As can be understood from the results, in the capacitor in Inventive Example 1, the presence of the niobium nitride layer 1b formed between the niobium substrate 1a and the dielectric layer 2 reduces the leakage current.

[0054]

(Inventive Examples 2 to 15)

In Inventive Examples 2 to 15, the correlation between the nitrogen content and leakage current was examined.

[0055]

Here, in Inventive Examples 2 to 15, the treatment

temperature in the nitriding step in the process of preparing a capacitor in Inventive Example 1 was changed in the range from 120℃ to 1000℃. The treatment temperatures in the nitriding step in Inventive Examples 2 to 15 were 120℃, 200℃, 250℃, 300℃, 600℃, 700℃, 800℃, 850℃, 870℃, 900℃, 920℃, 940℃, 970℃, and 1000℃, respectively. The other conditions were the same as those of Inventive Example 1. Note that the capacitor in Inventive Example 6 was the same as the capacitor prepared in Inventive Example 1.

[0056]

(Evaluation)

For the capacitors in Inventive Examples 2 to 15, the nitrogen content, leakage current, and compounds identified by X-ray powder method are given in Table 2.

[0057]

Note that the respective the leakage current measurement results of the solid electrolytic capacitors of the inventive examples 2 to 15 are normalized by the leakage current measurement result of the solid electrolytic capacitor of the inventive example 1 as 100,and the normalized the leakage current values are represented in

[0058]

[Table 2]

	leakage current	treatment temp. (℃)	nitrogen content (wt%)	identified compounds

Inventive Example 2	450	120	0.0005	Nb
Inventive Example 3	350	200	0.00075	Nb
Inventive Example 4	300	250	0.00085	Nb、Nb_2N
Inventive Example 5	120	300	0.001	Nb、Nb_2N
Inventive Example 6	100	600	0.02	Nb、Nb_2N
Inventive Example 7	105	700	0.05	Nb、Nb_2N
Inventive Example 8	110	800	0.08	Nb、Nb_2N
Inventive Example 9	170	850	0.09	Nb、Nb_2N
Inventive Example 10	180	870	0.12	Nb、Nb_2N
Inventive Example 11	195	900	0.17	Nb、Nb_2N
Inventive Example 12	200	920	0.20	Nb、Nb_2N
Inventive Example 13	400	940	0.22	Nb、Nb_2N、NbN
Inventive Example 14	450	970	0.25	Nb、Nb_2N、NbN
Inventive Example 15	550	1000	0.45	Nb、Nb_2N、NbN

[0059]

As can be seen from Table 2, the nitrogen content increases as the treatment temperature increases. Therefore, the nitrogen content can be controlled by adjusting the treatment temperature.

[0060]

As the nitrogen content is in the range from 0.001 wt% to 0.20 wt%, the leakage current is sufficiently reduced. As the nitrogen content is in the range from 0.001 wt% to 0.08 wt%, the leakage current is considerably reduced.

[0061]

Therefore, the nitrogen content is preferably not less than 0.001 wt% nor more than 0.20 wt%, more preferably not less than 0.001 wt% nor more than 0.08 wt%. The treatment temperature is preferably not lower than 300℃ nor higher than

920℃, more preferably not lower than 300℃ nor higher than 800℃.

[0062]

When the nitrogen content was in the range from 0.00085 wt% to 0.20 wt%, Nb and Nb_2N were detected. Meanwhile, when the nitrogen content was not less than 0.22 wt%, Nb, Nb_2N, and NbN were detected.

[0063]

As can be seen from the above, when the niobium nitride layer 1b includes Nb_2N, the leakage current is reduced, and when the niobium nitride layer 1b contains NbN, the leakage current is less effectively reduced. It is assumed that this is because Nb_2N has higher heat resistance than NbN, and can sufficiently prevent oxygen in the dielectric layer 2 from partly diffusing into the niobium substrate 1a.

[Brief Description of the Drawings]

[Fig. 1] A view of a solid electrolytic capacitor according to a first embodiment of the invention;

[Fig. 2] A sectional view of the anode and dielectric of a capacitor in Inventive Example 1;

[Fig. 3] A graph showing a measurement result by ESCA for a capacitor in Inventive Example 1;

[Fig. 4] A graph showing a measurement result by ESCA for a capacitor in Comparative Example 1;

[Fig. 5] A graph showing a measurement result by ESCA

for a capacitor in Comparative Example 2; and

[Fig. 6] A schematic view for use in illustration of a method of measuring leakage current in the capacitor in Inventive Example 1.

[Description of Reference Numerals]

1 anode

1a niobium substrate

1b nitride layer

2 dielectric layer

3 conductive polymer layer

4 carbon layer

5 silver paint layer

6 conductive adhesive

7 anode terminal

8 cathode terminal

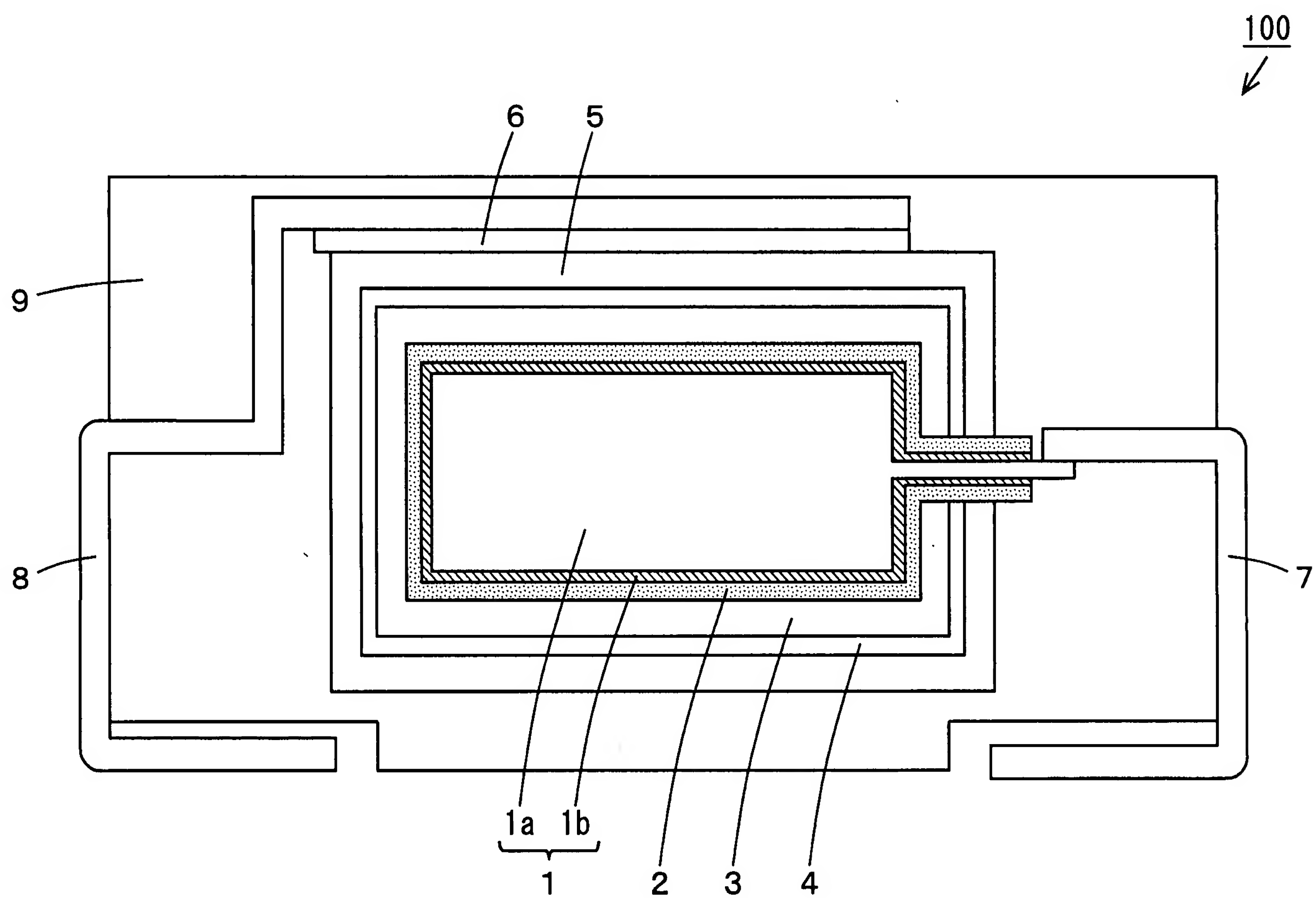
9 mold sheath resin

40 phosphoric acid aqueous solution

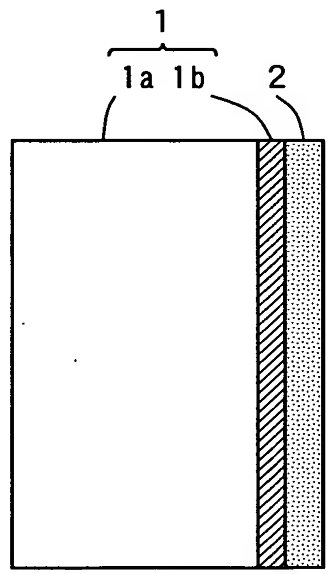
42 container

100 electrolytic capacitor

FIG. 1



F I G. 2



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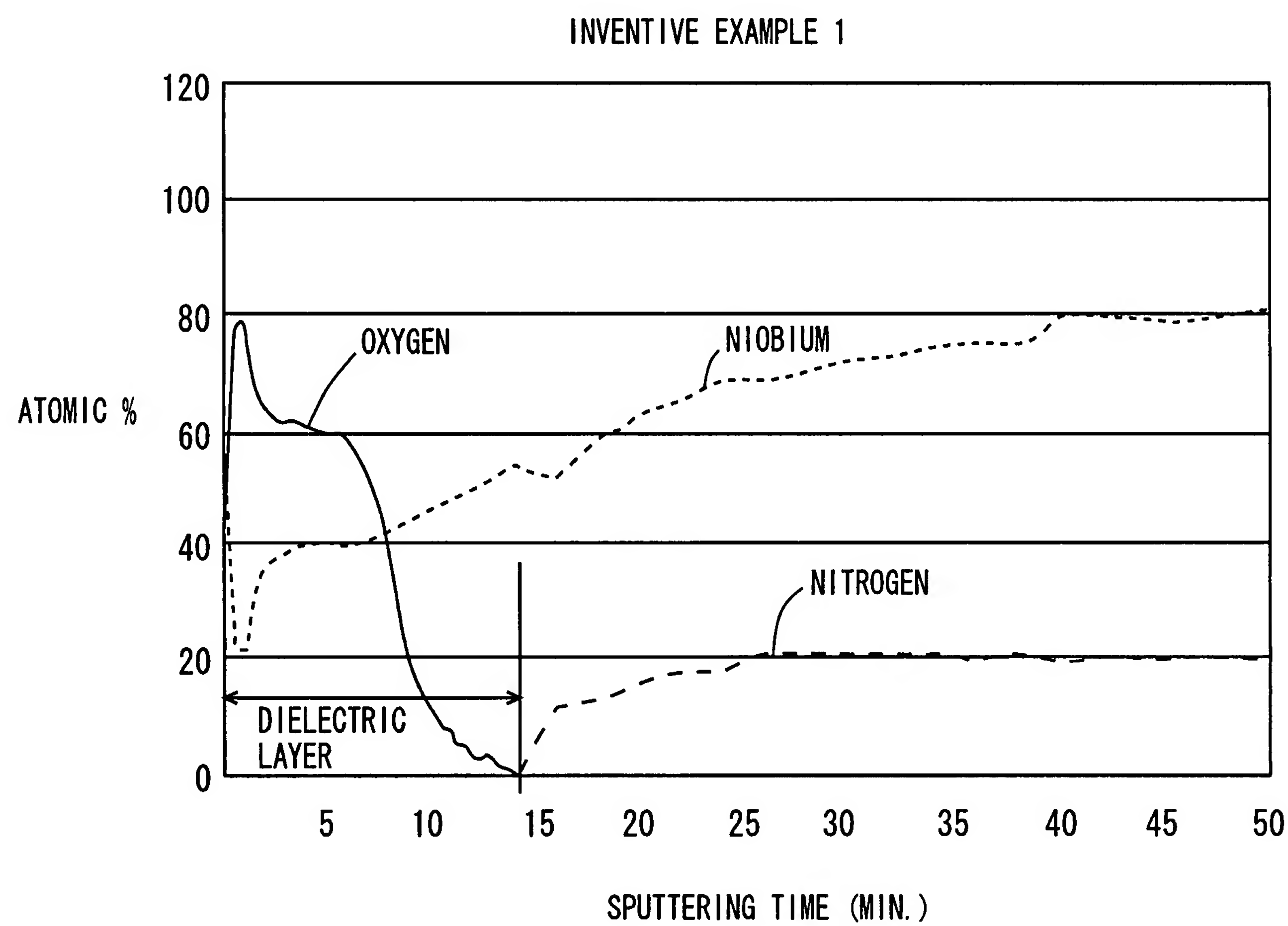
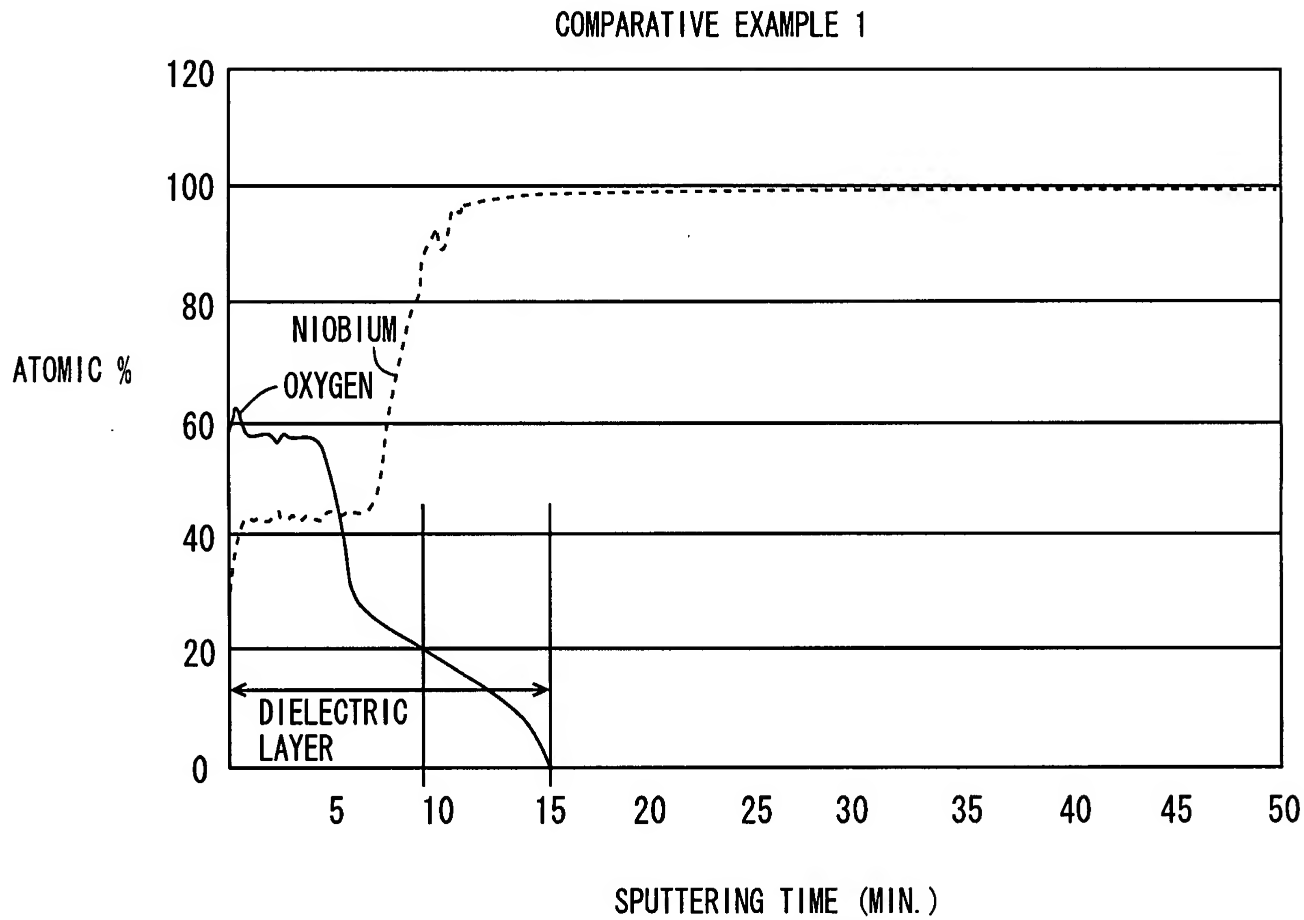
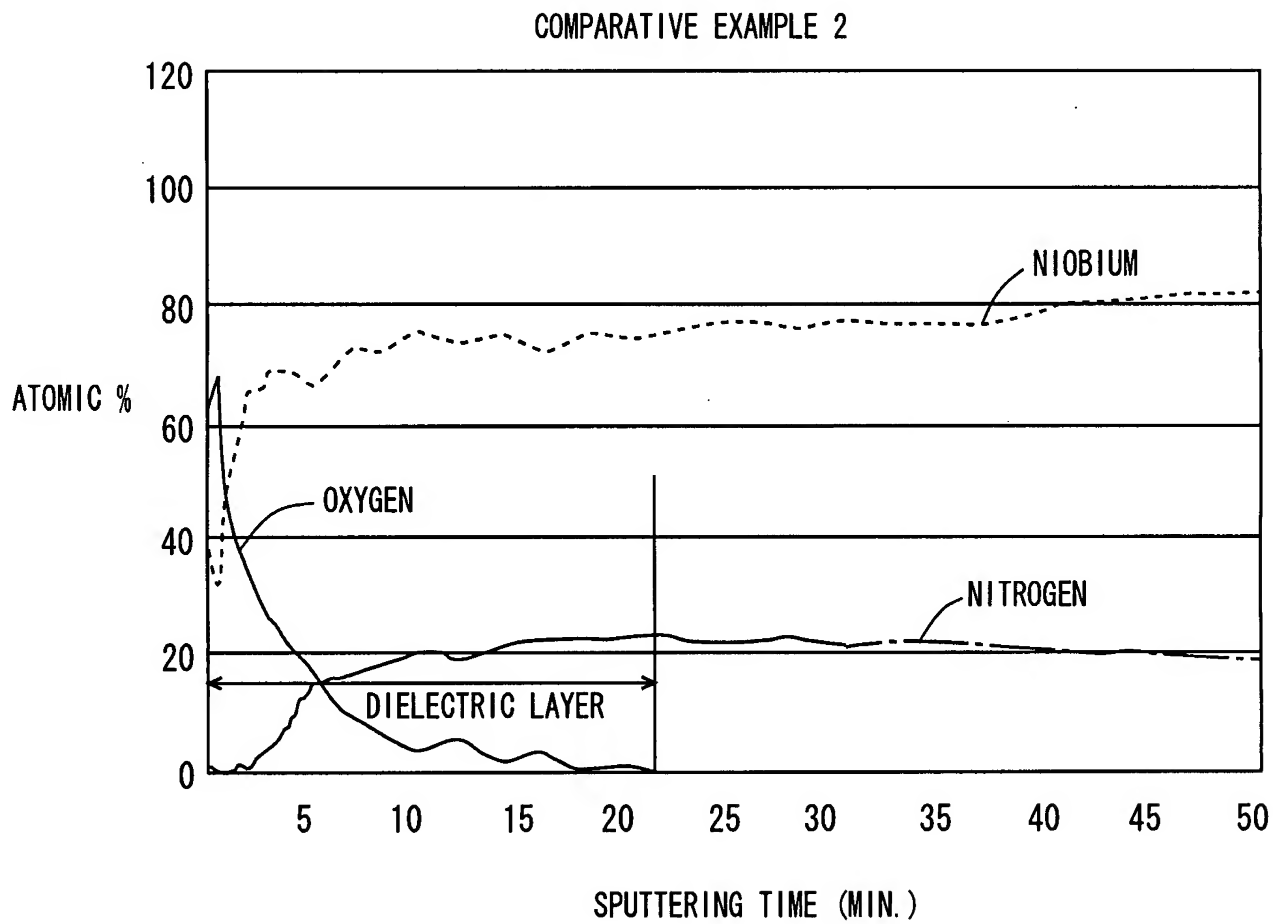


INVENTIVE EXAMPLE 1
ATOMIC %
120
100
80
60
40
20
0
OXYGEN
NIOBIUM
NITROGEN
DIELECTRIC LAYER
5
10
15
20
25
30
35
40
45
50
SPUTTERING TIME (MIN.)

F I G. 4

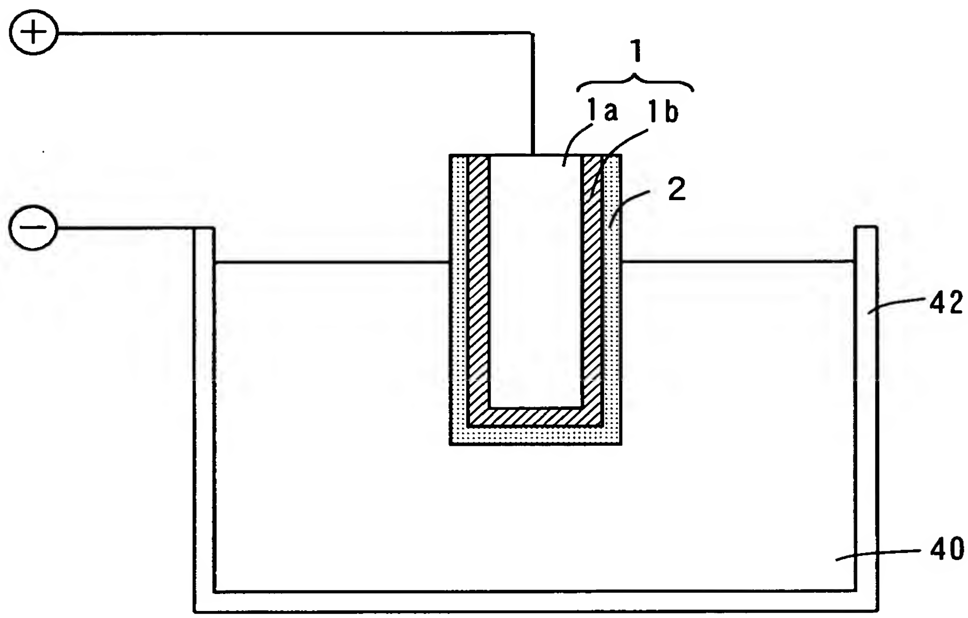

COMPARATIVE EXAMPLE 1
ATOMIC %
120
100
80
60
40
20
0
NIOBIUM
OXYGEN
DIELECTRIC
LAYER
5
10
15
20
25
30
35
40
45
50
SPUTTERING TIME (MIN.)

F I G. 5



COMPARATIVE EXAMPLE 2
ATOMIC %
120
100
80
60
40
20
0
NIOBIUM
OXYGEN
NITROGEN
DIELECTRIC LAYER
5
10
15
20
25
30
35
40
45
50
SPUTTERING TIME (MIN.)

F I G. 6



[Document Name] Abstract

[Abstract]

[Subject] To provide a solid electrolytic capacitor with reduced leakage current and a manufacturing method thereof.

[Solving Means] A solid electrolytic capacitor 100 has an anode 1 composed of a niobium substrate 1a and a niobium nitride layer 1b, and a dielectric layer 2 composed of niobium oxide is formed on the surface of the niobium nitride layer 1b. In the solid electrolytic capacitor 100, the nitrogen content based on the total weight of the niobium substrate 1a, the niobium nitride layer 1b, and the dielectric layer 2 is preferably not less than 0.001% by weight nor more than 0.2% by weight

[Selected Drawing] Fig. 1